From Glycerol to Value-Added Products

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Dedicated to Dr. Arjan de Nooy on the occasion of his 40th birthday

Today, industrial plants that produce glycerol are closing down and others are opening that use glycerol as a raw material, owing to the large surplus of glycerol formed as a by-product during the production of biodiesel. Research efforts to find new applications of glycerol as a low-cost feedstock for functional derivatives have led to the introduction of a number of selective processes for converting glycerol into commercially valued products. This Minireview describes a selection of such achievements and shows how glycerol will be a central raw material in future chemical industries.

1. Introduction

Glycerol (1,2,3-propanetriol or glycerine), an organic molecule isolated by heating fats in the presence of ash (to produce soap) as early as 2800 BC,[1] is an industrial chemical with tens of applications (Figure 1). Since the late 1940s, and following the discovery of synthetic surfactants, glycerol has been produced from epichlorohydrin obtained from propylene (and thus from fossil oil) as large chemical companies forecasted a glycerol shortage and initiated its synthetic production.[2] Today, however, glycerol plants are closing and others are opening that use glycerol as a raw material (including for the production of epichlorohydrin itself)[3] as a result of the large surplus of glycerol that is formed as a by-product (10% in weight) in manufacturing biodiesel fuel by transesterification of seed oils with methanol. To illustrate the trend, the global glycerol market was 800000 tons in 2005 with 400000 tons from biodiesel in comparison to 60000 tons only in 2001.[4]

Over the last decade, biodiesel has emerged as a viable fuel and as a fossil diesel additive to replace sulfur, whose content is being progressively lowered according to tighter environmental legislation. Until the recent increases in petroleum prices, high production costs made biofuels unprofitable without government subsidies. However, the increasing production of biodiesel is not artificially sustained and is predicted to spread and increase, as biodiesel provides sufficient advantages to merit subsidy.[5] Besides the closure of production plants, industry reacted to this situation by starting research to find new applications of glycerol as a low-cost feedstock for functional derivatives either for mass consumption, such as additives for concrete,[6] or as a precursor of valued fine chemicals.

With a focus on recent developments in the conversion of glycerol into value-added chemicals, we describe in this Minireview how the "new" chemistry of glycerol will play a crucial role in future biorefineries[7] (Scheme 1), as its

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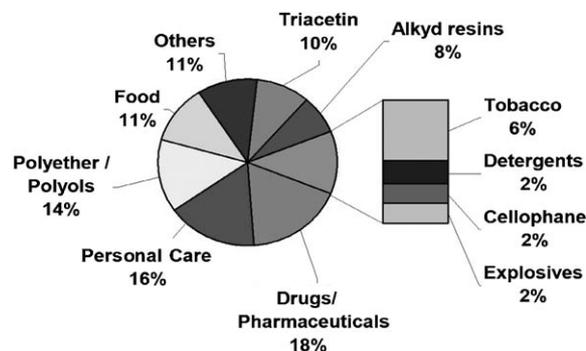1-4-8 Higashi Minato, Kokura-Kita-ku
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Figure 1. The market for glycerol (volumes and industrial use). Source: Novaol, May 2002.
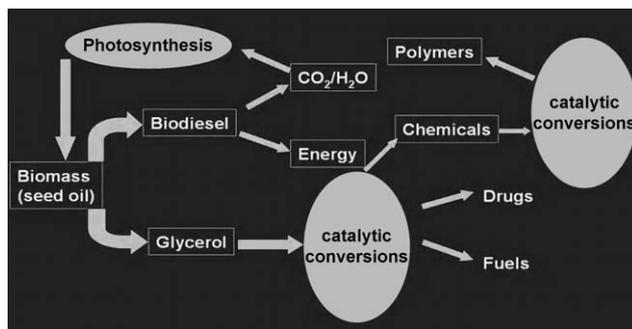
derivatives find use in sectors as diverse as fuels, chemicals, automotive, pharmaceutical, detergent, and building industries.

2. Catalytic Conversion of Glycerol

A selection of the chemicals that can be obtained using glycerol as reaction substrate are illustrated in Scheme 2.

2.1. Selective Oxidation

All glycerol oxygenates derivatives are of practical value. However, the extensive functionalization of the triol molecule with similarly reactive hydroxy groups renders its selective oxidation particularly difficult.[8] The oxidation of primary hydroxy groups yields glyceric acid and further tartronic acid, which are both commercially useful compounds. Oxidation of the secondary hydroxy group yields the important fine chemical dihydroxyacetone (DHA), whereas the oxidation

Scheme 1. The chemistry of glycerol will play a crucial role in future biorefineries, in which materials and energy will be produced from renewable raw materials.

of all three hydroxy groups affords the highly functionalized molecule ketomalonic (or mesoxalic) acid.

2.1.1. Oxidation of the Primary Hydroxy Groups

The aerobic oxidation of glycerol in water over conventional precious-metal-based catalysts such as Au/C and Pt/C yields glyceric acid. Carbon-supported Au catalyzes the oxidation of glycerol to sodium glycerate with 92 % selectivity at full conversion,[9] whereas Pt/C at 50 °C yields glyceric acid with a maximum 70 % yield at pH 11.[10,11]

Pt supported over CeO_2 catalyzes the oxidation of both primary hydroxy groups to give tartronic acid in 40 % yield.[12] Oxidative dehydrogenation over supported noble-metal catalysts, however, generally suffers from a low stability of the supported metals in the oxidative environment and requires a thorough control of the reaction conditions to minimize the formation of undesired by-products. On the contrary, the

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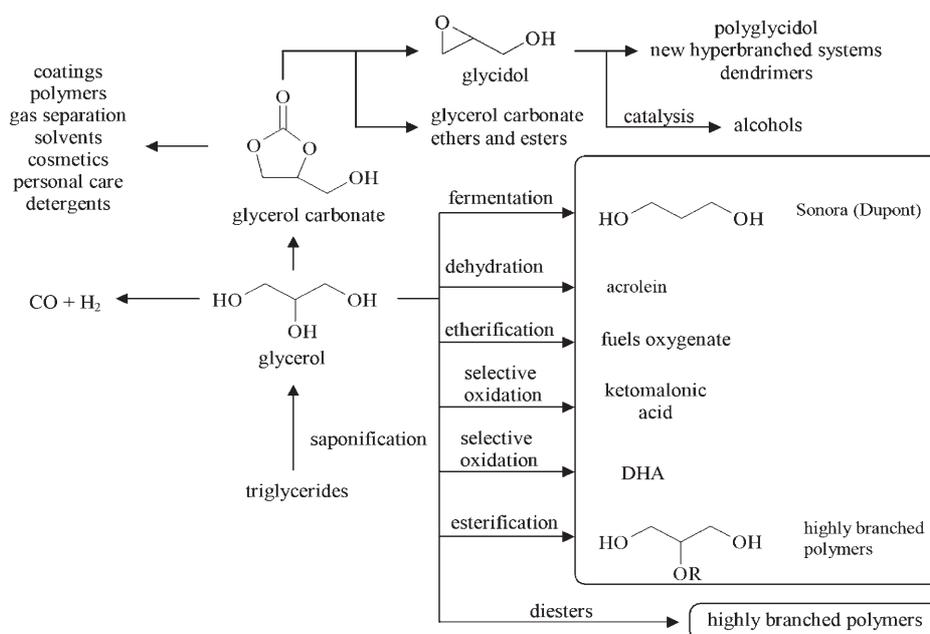
Hiroshi Kimura was born in 1948 in Japan. He received his MSc in chemistry in 1973 and his PhD in 1997 from Kyushu University (Hukuoka). He then worked at Kao Corp. (Wakayama) on the development of metal-based catalysts for glycerol chemistry. He is currently a research chemist at Kokura Synthetic Industries in Hukuoka.

Michele Rossi, born in 1939 in Milan (Italy), graduated in industrial chemistry at the University of Milan in 1963. In 1974 he was appointed a professor of inorganic chemistry at the University of Bari, and he has held a similar position at the University of Milan since 1988. His research is focused on metal-based catalysis and resulted in the discovery of nitrogen fixation.

Cristina Della Pina completed her undergraduate studies in chemistry at the University of Milan in 2003 and went on to complete her PhD there in 2006 under the guidance of Professor Rossi. She is currently a research fellow in the same group, focusing on the development of novel gold catalysts for selective oxidation.
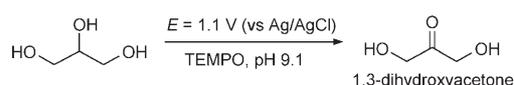
Scheme 2. Glycerol as a platform for functional chemicals (see text for details).

organic nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperi-din-1-oxyl) is a selective catalyst for both the homogeneous and heterogeneous oxidation of all the hydroxy groups of glycerol and thus affords high yields of ketomalonic acid in one pot using NaOCl as a stoichiometric oxidant.[13]

2.1.2. Oxidation of the Secondary Hydroxy Groups

DHA is the main active ingredient in all sunless tanning skincare preparations and is currently produced (with a global market of about 2000 tons per year) by microbial fermentation of glycerol over *Gluconobacter oxydans*. A clean and direct conversion of glycerol into DHA by anodic oxidation in the presence of catalytic TEMPO was, however, only recently introduced (Scheme 3).[14]

Scheme 3. One-pot oxidation of glycerol to 1,3-dihydroxyacetone is achieved by simply applying an electric potential to a glycerol solution in the presence of catalytic TEMPO.

The process gives yields (25%) that are comparable to that of the cumbersome biotechnological process used in industry in the absence of a competitive chemical process. However, no stoichiometric chemical oxidant is used throughout the whole process and the radical TEMPO can be entirely recovered at the end of the reaction by simple extraction.[15]

2.1.3. Oxidative Polymerization

When a single multifunctional supported CeBiPt/C catalyst is used either under basic[16] or acidic[17] conditions,

glycerol is directly converted into poly(ketomalonate) (PKM) in an elegant one-pot oxidative polymerization process to afford a high-molecular-weight polycarboxylate that is an excellent building block for household detergents. Along with hydration, polymerization of the generated ketomalonate (KM) to PKM is the energy relaxation process for the active ketone form of KM and is based on the high dipole of its ketone carbonyl group—a functional unit that is prone to polymerization similar to that observed in the case of formaldehyde. The PKM thereby formed can easily be decomposed with excess aeration, which results in full decarboxylation and formation of poly(oxymethylene).[17]

2.2. Etherification: Fuel Oxygenates

Glycerol cannot be added directly to fuel because at high temperatures it polymerizes—and thereby clogs the engine—and it is partly oxidized to toxic acrolein. On the other hand, oxygenated molecules such as methyl tertiary butyl ether (MTBE) are used as valuable additives as a result of their antidetonant and octane-improving properties. In this respect, glycerol tertiary butyl ether (GTBE) is an excellent additive with a large potential for diesel and biodiesel reformulation. In particular, a mixture of 1,3-di-, 1,2-di-, and 1,2,3-tri-*tert*-butyl glycerol, when incorporated in standard 30–40% aromatic-containing diesel fuel, leads to significantly reduced emissions of particulate matter, hydrocarbons, carbon monoxide, and unregulated aldehydes.[18] Such alkyl ethers are easily synthesized: glycerol is reacted with isobutylene in the presence of an acid catalyst, and the yield is maximized by carrying out the reaction in a two-phase reaction system, with one phase being a glycerol-rich polar phase (containing the acidic catalyst) and the other phase being an olefin-rich hydrocarbon phase from which the product ethers can be

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readily separated.[19] On the other hand, if the reaction is carried out over an amberlyst resin, methanol in the crude glycerol must be removed to avoid catalyst poisoning.[20] In an aim to replace toxic MTBE,[21] the optimization of glycerol ether formulations based on the results of engine tests is currently carried out in Europe and in the US, where recently also dibutoxy glycerol was shown to act as an excellent fuel oxygenate.[22]

2.3. Hydrogenolysis: Propylene Glycol

Glycerol is a polyol and thus competes with other polyols on the market.[23] A remarkable conversion of crude glycerol into propylene glycol (1,2-propanediol), however, was recently introduced which resulted in an antifreeze product (70% propylene glycol and 30% glycerol) that can be produced, refined, and marketed directly by existing biodiesel facilities.[24] The method is based on hydrogenolysis (i.e. dehydration followed by hydrogenation) of glycerol over a copper chromite catalyst (CuCr$_2$O$_4$) at 200°C and less than 10 bar (versus about 260°C and more than 150 bar for other systems) coupled with a reactive distillation.[25]

The reaction pathway proceeds via an acetol (hydroxyacetone) intermediate in a two-step process. The first step of forming acetol occurs at atmospheric pressure, while subsequent hydrogenation at 200°C and 10 bar H$_2$ eventually affords propylene glycol in 73% yield at significantly lower cost than propylene glycol made from petroleum. A main advantage of the process is that the copper–chromite catalyst can be used to convert crude glycerol without further purification (whereas supported noble-metal catalysts are easily poisoned by contaminants such as chloride).[26] Finally, the hydroxyacetone (acetol) formed as an intermediate is an important monomer used in industry to make polyols, thus the process opens up more potential applications and markets for products made from glycerol.
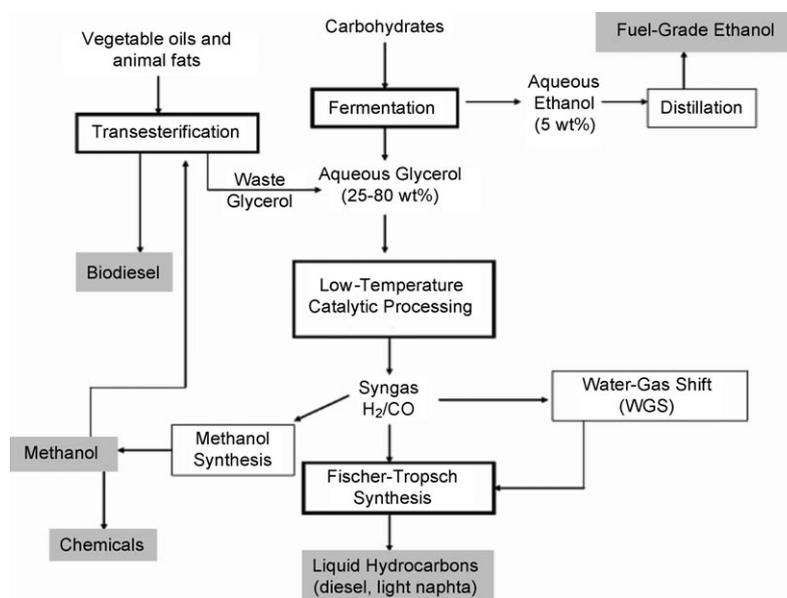
2.4. Dehydration: Acrolein

Acrolein is a versatile intermediate largely employed by the chemical industry for the production of acrylic acid esters, superabsorber polymers, and detergents. It can be obtained from glycerol in excellent yield by using a method introduced in the mid-1990s which is based on glycerol dehydration on acidic solid catalysts. Hence, passing a glycerol–water gas mixture at 250 to 340°C over an acidic solid catalyst with a Hammett acidity function of less than −2 results in full conversion of glycerol into acrolein.[27] The process was not commercialized owing to its poor economics compared to a commercial production route based on the oxidation of propylene with a Bi/Mo mixed oxide catalyst. Most recently,

the usage of sub- and supercritical water as the reaction media has been investigated but, again, the conversion and acrolein selectivities achieved so far do not satisfy the criteria of an economical process.[28]

2.5. Reforming: Syngas

From both industrial and innovation viewpoints, the major achievement of the new chemistry of glycerol is the reforming process in which glycerol in the aqueous phase is converted into hydrogen and carbon monoxide (synthesis gas or syngas) under relatively mild conditions (225–300°C) by using a platinum-based catalyst in a single reactor.[29] Such formation of synthetic gas is crucial for the future of biorefineries because syngas can be used as a source for fuels and chemicals by Fischer–Tropsch or methanol syntheses (Scheme 4).

Scheme 4. Schematic view of liquid fuel and chemical production through catalytic processing of glycerol (reproduced from Ref. [29], with permission).

Moreover, glycerol (advantageously obtained by the fermentation of glucose)[30] offers an energy-efficient alternative to ethanol-based products because higher product concentrations can be formed. Careful selection of the Pt catalyst allows the ratio of the gases produced in the degradation of glycerol to be adjusted to the 2:1 value suitable for the Fischer–Tropsch process by minimizing the extent of the water gas shift reaction (reducing the concentration of water in the feed).

The energy balance for these coupled reactions is also favorable. The formation of synthesis gas from glycerol is highly endothermic, with an enthalpy change of about 80 kcal mol^{-1}, but the conversion of synthesis gas to alkanes is highly exothermic (−110 kcal mol^{-1}), such that the overall conversion of glycerol into alkanes by the combination of reforming and Fischer–Tropsch synthesis is mildly exother-

mic, with an overall gain in energy of −30 kcal per mole of glycerol.

2.6. Fermentation to 1,3-Propanediol

Glycerol can serve as a feedstock for the fermentative production of 1,3-propanediol, one of the two primary components (the other is terephthalic acid) of Sonora and Corterra fibers, a polyester with excellent potential for use in textiles and carpeting that has been dubbed the "new nylon". Fermentation uses bacterial strains in the groups *Citrobacter*, *Enterobacter*, *Ilyobacter*, *Klebsiella*, *Lactobacillus*, *Pelobacter*, and *Clostridium*.[31] In each case, glycerol is converted into 1,3-propanediol in a two-step, enzyme-catalyzed reaction sequence. In the first step, a dehydratase catalyzes the conversion of glycerol into 3-hydroxypropionaldehyde (3-HPA) and water [Eq. (1)]. In the second step, 3-HPA is reduced to 1,3-propanediol by a nicotinamide adenine dinucleotide (NAD$^+$)-linked oxidoreductase [Eq. (2)], whose oxidized form partly oxidizes glycerol to DHA [Eq. (3)]. The 1,3-propanediol is not metabolized further and, as a result, accumulates in the media. The overall reaction consumes a reducing equivalent in the form of the cofactor, NADH, which is oxidized to NAD$^+$.

$$glycerol \rightarrow 3\text{-}HPA + H_2O \tag{1}$$

$$3\text{-}HPA + NADH + H^+ \rightarrow 1,3\text{-}propanediol + NAD^+ \tag{2}$$
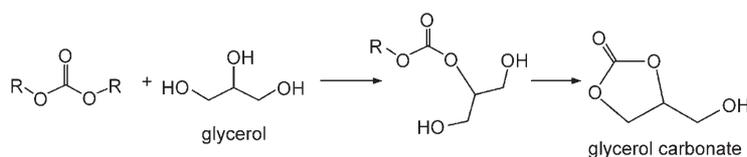
$$glycerol + NAD^+ \rightarrow DHA + NADH + H^+ \tag{3}$$

As such, this biological process for the production of 1,3-propanediol has a low metabolic efficiency and uses relatively expensive glycerol,[32] but a less costly production of 1,3-propanediol can be achieved by using glucose as optimal substrate thus combining the pathway from glucose to glycerol[30] successfully with the bacterial route from glycerol to 1,3-propanediol.[33]

2.7. Glycerol Carbonate

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is a relatively new material in the chemical industry with a large potential as a novel component of gas-separation membranes, a solvent for several types of materials, and biolubricant owing to its adhesion to metallic surfaces and resistance to oxidation, hydrolysis, and pressure. It can be prepared directly and in high yield from renewable glycerol and dimethyl carbonate in a reaction catalyzed by lipases (Scheme 5).
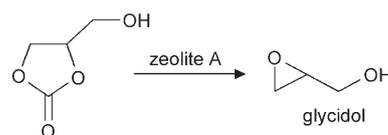
Inexpensive glycerol carbonate could serve as a source of new polymeric materials such as glycidol, a high-value component in the production of a number of polymers. Glycidol is easily obtained in high yield (86 % and 99 % purity at 35 mbar and 180 °C) from glycerol carbonate by catalytic reaction, involving rapid contraction of the five-membered

Scheme 5. Glycerol carbonate may be formed from the reaction of a dialkyl carbonate with glycerol, with an intermediate that undergoes a second esterification.

cyclic carbonate unit into the three-membered cyclic epoxy unit, within the pores of zeolite A (Scheme 6).

Besides it being a high-value component in the production of epoxy resins and polyurethanes, glycidol can be polymer-

Scheme 6. Glycidol forms easily from glycerol carbonate, catalyzed by zeolite A (or γ-alumina) under reduced pressure.

ized into a polyether polyol called polyglycerol.[34] Its high functionality, together with the versatile and well-investigated reactivity of its hydroxy functions, is the basis for a variety of derivatives. Indeed, a variety of polyglycerols were eventually commercialized for applications that range from cosmetics to controlled drug release.[35]

2.8. Epichlorohydrin

Epichlorohydrin, a chemical employed in the production of epoxy resins, is now commercially synthesized from glycerol by a catalytic reaction with HCl followed by dehydrochlorination with NaOH. The glycerol-based process (named Epicerol) involves the direct synthesis of dichloropropanol, an intermediate product, from glycerine and hydrochloric acid. Thus, natural glycerol is used as a substitute for the propylene feedstock employed in the traditional epichlorohyrin production process, involving formation of allyl chloride by reaction of propylene with Cl$_2$. Overall, the Epicerol process uses a combination of undisclosed metal catalysts and requires a lower specific consumption of chlorine and water, thereby reducing chlorinated effluents.[36]

3. Outlook and Conclusions

As described in this Minireview, glycerol is emerging as a versatile bio-feedstock for the production of a variety of chemicals, polymers, and fuels. Whether as solvent, antifreeze, detergent, monomer for textiles, or drug, new catalytic conversions of glycerol have been discovered that are finding application for the synthesis of products whose use ranges from everyday life to the fine-chemicals industry. Results include processes that are capable of converting crude

glycerol into antifreeze on site, thus avoiding unnecessary transportation, direct conversion of glycerol into valued dihydroxyacetone by mild anodic oxidation, and the high-yield production of syngas ($H_2 + CO$). With current (high) oil prices and faced with increasing demand from emerging economies worldwide, the production of glycerol will only increase, resulting in ever lower prices of this product and in the spread of biorefineries that use glycerol (as such or derived from glucose) as a feedstock for the synthesis of organic compounds. We may envisage a near future when syngas obtained from glycerol will be used to synthesize a variety of hydrocarbons, or when 1,3-propanediol obtained enzymatically from glycerol will be employed in the production of high-performance polyesters. By highlighting the basic advances on which these processes are based, we hope to have shown how a number of practical limitations posed by glycerol chemistry, such as the low selectivity encountered when employing traditional stoichiometric and older catalytic conversions, were actually solved based on the understanding of the fundamental chemistry of glycerol.
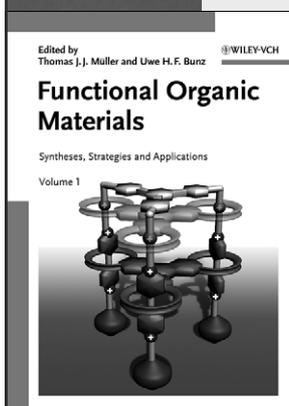
[1] J. A. Hunt, *Pharm. J.* **1999**, *263*, 985.

[2] See the recent report from Frost & Sullivan: "R&D Creating New Avenues for Glycerol" (August 4, 2006), available online at https://www.frost.com/prod/servlet/market-insight-top.pag?docid = 77264824.

[3] The US agribusiness company Archer Daniels Midland recently announced plans to make propylene glycol from glycerol instead of propylene oxide. Dow Chemical closed its glycerol plant in Texas early this year when Procter & Gamble Chemicals shut down a natural glycerol refinery in England. See: a) M. McCoy, *Chem. Eng. News* **2006**, *84*(6), 7; b) M. McCoy, *Chem. Eng. News* **2006**, *84*(2), 32.

[4] As of July 2006, pure glycerol was sold at 600–800 €/ton while crude glycerol of high quality obtained by biodiesel production was sold at 600–700 €/ton with glycerol currently priced at around 850 USD/ton. At prices approaching 770 USD/ton, glycerol becomes a significant platform chemical. If, as anticipated, biodiesel production grows to 3.23 million tons worldwide, an extra 323 000 tons of glycerol would reach the market thus rendering glycerol a readily available commodity.

[5] Biodiesel yields a net energy balance ratio of 1.93 (i.e. 93 % more energy produced than the energy invested in its production, whereas ethanol yields only 25 % more energy): J. Hill, E. Nelson, D. Tilman, S. Polasky, D. Tiffany, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 11 206.

[6] Crude glycerol from biodiesel production is an excellent additive for concrete, enhancing its resistance to compression and grinding and lowering its setting time. Mechanical tests carried out on "clinker" (the cement precursor which is mixed with gypsum to yield the concrete) samples doped with crude glycerol show, in all cases, that raw glycerol imparts better mechanical and chemical properties compared to those samples doped with commercial additives, including pure glycerol. Tests on an industrial scale using trucks of crude glycerol confirmed the results on the laboratory scale, and commercialization of cement added with biodiesel glycerol started in late 2006. M. Rossi, M. Pagliaro, R. Ciriminna, C. Della Pina, W. Kesber, WO2006051574, **2004**.

[7] A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry. For a thorough discussion of the topic, see: http://www.nrel.gov/biomass/biorefinery.html; see also the recent overview: J. H. Clark, V. Budarin, F. E. I. Deswarte, J. J. E. Hardy, F. M. Kerton, A. J. Hunt, R. Luque, D. J. Macquarrie, K. Milkowski, A. Rodriguez, O. Samuel, S. J. Tavener, R. J. White, A. J. Wilson, *Green Chem.* **2006**, *8*, 853.

[8] For example, as in the case of conversion with H_2O_2 over metallosilicate catalyst when formaldehyde, formic acid, and CO_2 are the main products: P. McMorn, G. Roberts, G. J. Hutchings, *Catal. Lett.* **1999**, *63*, 193.

[9] a) S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely, C. A. Attard, G. J. Hutchings, *Top. Catal.* **2004**, *27*, 131; b) S. Demirel-Gulen, M. Lucas, P. Claus, *Catal. Today* **2005**, *102*, 166.

[10] R. Garcia, M. Besson, P. Gallezot, *Appl. Catal. A* **1995**, *127*, 165.

[11] N. Dimitratos, J. A. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati, A. Villa, *Catal. Lett.* **2006**, *108*, 147.

[12] Under basic conditions: a) P. Gallezot, *Appl. Catal. A* **1995**, *133*, 179; b) H. Kimura, Jpn. Pat. Application, 95253, **1993**; under acidic conditions: c) H. Kimura, Jpn. Pat. Application, 253062, **1994**; d) H. Kimura, Jpn. Pat. Application, 315624, **1994**.

[13] R. Ciriminna, M. Pagliaro, *Adv. Synth. Catal.* **2003**, *345*, 383. As the dihydrate calcium salt, ketomalonate is a potent hypoglycemic agent commercialized in diabetes therapy while in general ketomalonic acid is a versatile synthon for organic chemistry.

[14] R. Ciriminna, G. Palmisano, C. Della Pina, M. Rossi, M. Pagliaro, *Tetrahedron Lett.* **2006**, *47*, 6993.

[15] Earlier reported metal-based oxidative dehydrogenation of glycerol over a supported Bi-Pt catalyst to afford an optimized maximum yield of 37 % at 70 % glycerol conversion (H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi, Y. Inaya, *Appl. Catal. A* **1993**, *96*, 217) has not found practical application.

[16] a) H. Kimura, *J. Polym. Sci. Part A* **1998**, *36*, 195; b) H. Kimura, *J. Polym. Sci. Part A* **1996**, *34*, 3595.

[17] H. Kimura, *Recent Res. Dev. Polym. Sci.* **1999**, *3*, 327.

[18] F. J. Liotta, Jr., L. J. Karas, H. Kesling, US Patent 5308365, **1994**.

[19] V. P. Gupta, US Patent 5476971, **1995**.

[20] H. Noureddini, W. R. Dailey, B. A. Hunt, "Production of Ethers of Glycerol from Crude Glycerol" **1998**. Paper posted at DigitalCommons at the University of Nebraska-Lincoln: http://digitalcommons.unl.edu/chemeng_biomaterials/18/.

[21] By the Netherlands-based consortium Procedé Group bv, with the involvement of industrial partners. According to an EU directive, by the year 2010 5.75 % of the total amount of fuel consumed in the EU should originate from renewable sources. In Germany alone, this would mean 30 million tons, equivalent to 3 million tons of glycerol or to 10 millions tons of GTBE (a likely antidetonant). If realized, it could be easily absorbed by the market, as large amounts of TBE are already available on the market as it used as the starting material of MTBE still in the EU (but it is banned in California and 19 other US states).

[22] J. Spooner-Wyman, D. B. Appleby, "Heavy-Duty Diesel Emissions Characteristics of Glycerol Ethers", 25th Symposium on Biotechnology for Fuels and Chemicals, Breckenridge, Colorado **2003**: http://www.nrel.gov/biotechsymp25/session5_pp.html.

[23] For instance, NOF Corporation in Japan recently developed a new antifreeze (Camag) composed of glycerol and potassium

acetate to prevent freezing of roads in the cold northern district of Japan.

[24] For this achievement, Professor G. J. Suppes was awarded the 2006 Presidential Green Chemistry Challenge Awards: http://www.epa.gov/greenchemistry/pubs/pgcc/winners/aa06.html. Polyol Partners can also hydrocrack glycerol and form propylene glycol: C. Boswell, *Chemical Marketing Reporter*, January 24, 2005.

[25] M. Dasari, P. Kiatsimkul, W. Sutterlin, G. J. Suppes, *Appl. Catal. A* **2005**, *281*, 225.

[26] For example, as in the case of Ru/C coupled to an acid catalyst such as ion-exchange resin amberlyst, which is effective in the hydrogenolysis of glycerol under mild reaction conditions (393 K, 8.0 MPa): T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, *J. Catal.* **2006**, *240*, 213.

[27] W. Girke, H. Klenk, D. Arntz, T. Haas, A. Neher, US Patent 5387720, **1995**.

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[33] D. Liu, "Integrated Production for Biodiesel and 1,3-Propanediol with Lipase-Catalyzed Transesterification and Fermentation". Presentation at the Japanese Institute of Energy, **2006**: http://www.jie.or.jp/pdf/21%5B1%5D.Prof.DehuaLIU.pdf#search=%22Liu%2Bpropanediol%22.

[34] G. Rokicki, P. Rakoczy, P. Parzuchowski, M. Sobiecki, *Green Chem.* **2005**, *7*, 529.

[35] Small-scale production of these highly branched glycidol polymers has been commercialized in Europe by Hyperpolymers (Germany).

[36] Solvay is building a facility utilizing this new process which should be operative in the first half of 2007, with the required glycerol supplied from the biodiesel producer Diester Industrie.